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Analysis by Raman and infrared spectroscopy combined with theoretical studies on the identification of plasticizer in PVC films

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A B S T R A C T

Raman and Fourier Transform infrared spectroscopy were used to study the vibrational spectra in commercial polyvinyl chloride (PVC) flexible films. In order to have insights of the PVC and the plasticizer structures, density functional theory calculations were conducted via B3LYP hybrid functional. The infrared and Raman calculations took into account geometry optimization of the PVC film, the plasticizer DEHA and the convolution of both. The convoluted spectra were then compared with the experimental data. Finally, the thermal stability of the PVC films was checked through one-hour thermal treatment of the samples comprising temperatures ranges from 50 to 200 °C.

1. Introduction

Polyvinyl chloride (PVC) is the word third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene [1]. In pure composition it has high stiffness and great degradation when exposed to sunlight or even near ambient temperatures. For using in most of commercial applications the poly (vinyl chloride) (PVC) requires the addition of plasticizers. The addition of the plasticizers to the PVC allows this polymer to be sold commercially as stretchable films used, for example, in food packaging and day-to-day cooking. The plasticizers are mainly composed of long carbon chains with substitution of oxygen atoms or aromatic groups, like phthalate. One example is the di-(2-ethylhexyl) adipate (DEHA) presented in Fig. 1 [2,3].

Under heat exposure, PVC films starts degradation processes connected with the production of hydrochloric acid and the consequent discoloration due the formation of conjugated double bonds [4–7]. In this context, vibrational spectroscopy plays a very important role in elucidating polymer structure and normal mode analysis. The advantage of Fourier-transform infrared (FT-IR) analysis is the ability for detecting functional groups, characterizing covalent bonding information and data interpretation for polymers [8]. FT-IR covers a wide range of chemical applications, especially for polymers and organic compounds. Used together with other analytical techniques, FT-IR can be very effective in the identification of unknown plastics and polymeric

materials [9].

Raman spectroscopy is one of the optical techniques capable to give a quantitative information about molecular orientation in polymers [10] and has been used in the study of commercial PVC films [3]. Furthermore, Raman spectroscopy is an appropriate tool for investigating thermally degraded PVC [7,11]. In addition, a precise determination of the structure can be made through quantum chemistry which combined with experimental data can be useful to determine vibrational bands [12]. These investigations have been extremely useful not only to rationalize the experimental observations but also to develop a comprehensive design of new food packaging materials by using the knowledge provided by such calculations. In the last decade many theoretical studies have been devoted to ab initio and/or density functional theory (DFT) methods [13]. Theoretical investigation of the thermal dehydrochlorination of PVC were presented by Wang et al. [14]. More recently Raman spectroscopy of the commonly used plasticizer dioctyl phthalate was reported on the literature [15]. However, more theoretical and experimental work focused on the identification of plasticizers in PVC doped materials is required concerning food security and environmental contamination.

In this work vibrational properties of PVC commercial films are analyzed by optical spectroscopies together with quantum chemical calculations by means of the density functional theory (DFT). The purpose of the study was to present a theoretical model of the PVC and
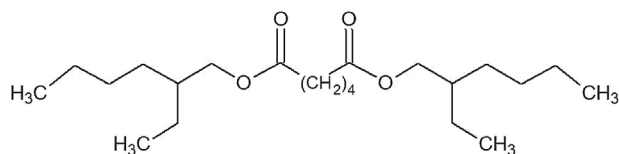
Fig. 1. Chemical structure of DEHA-di-(2-ethylhexyl) adipate.

apply infrared absorption spectroscopy and Raman scattering for the identification of commercial PVC films. The theoretical model allow us to predict the structural geometry as well as the identification of the vibrational modes of the substance. In addition the stability of the material under the effect of temperature was investigated by Raman / FT-IR spectra analysis with heat treatment of the samples at temperatures ranging from 50 to 200°, which lies within the normal heat operation of domestic ovens and microwaves. The comparisons between the theoretical and experimental results are also discussed.

2. Methods and calculations

2.1. Experimental

Sample preparation: Poly (vinyl chloride) films were acquired in local market. Samples were handled and received thermal treatment in a EDG/1800 muffle furnace during 1 h but no other chemical treatment and the tests were executed subsequently.

FT-IR measurements: The Fourier transform infrared spectroscopy (FT-IR) was recorded using a Bruker Tensor 27 FT-IR and OPUS Data Collection Program at a resolution of $4\,cm^{-1}$. The spectra were obtained in the range of $4000–400\,cm^{-1}$, submitted to 120 scans, aperture setting 2.5 mm and phase resolution equal to 32. The bands assignments were made for PVC/additives and the behaviour of main bands were analysed in order to evaluate chemical modifications on thermally treated samples.

Raman measurements: A T64000 spectrometer from Horiba Jobin Yvon was used to obtain the Raman spectra of the samples. A basic experimental setup was used to obtain the spectra, i.e., a subtractive double stage mode conjugated with a monochromator. All Raman measurements carried out on PVC samples were made keeping the same equipment configuration. The samples were excited with a Melles Griot Argon laser model 543-AP-01, tuned at 488 nm. The laser beam was focused on the sample by an Olympus BX41 confocal microscope with a $50\times/0.75$ objective and the scattered radiation collected by the microscope itself being analyzed in a Charge-Coupled Device (CCD) cooled with liquid nitrogen. The spectrometer acquisition and control process were performed by the Labspec software provided by the manufacturer of the apparatus. The spectral resolution was adjusted with a pinhole of 300×10^{-6} m and an acquisition time of 240 s, Slit 1: 200×10^{-6} m, Slit 2: 100×10^{-6} m. Measurements were performed at intervals: $1600–500\,cm^{-1}$ and $3100–2600\,cm^{-1}$.

2.2. Computational details

All of the DFT based calculations reported for PVC and plasticizer were carried out using the Orca software [16]. The input geometrical parameters used were obtained from the energy minimization carried out by molecular mechanics. The main calculations were performed using standard techniques with B3LYP functional [17,18] and the Split valence polarization (SVP) double-zeta basis set [19]. The B3LYP functional as implemented in Orca, has exchange correlation given by:

$$E_{xc} = (1 - a_0)E_x^{LDA} + a_0 E_x^{HF} + a_x E_x^{B88} + a_c E_c^{B3LYP88} + (1 - a_x)E_c^{VWN80}$$

(1)

where $a_0 = 0.2$, $a_x = 0.72$ and $a_c = 0.81$ while using a combination of Hartree-Fock (HF), local density approximation (LDA) and Becke-1988
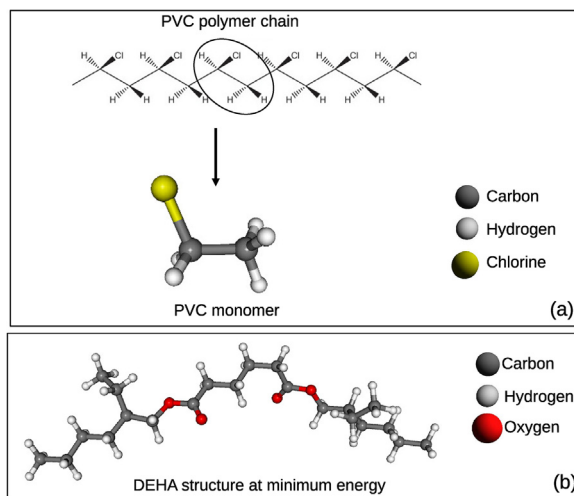

Fig. 2. (a) Structure used to represent the PVC in the theoretical model. (b) Optimized geometry for the DEHA plasticizer compound.

(B88) exchange energy. Additionally, Lee-Yang-Parr 1988 (LYP88) and Vosko, Wilks, Nusair 1980 (VWN) compose the correlation term of this hybrid functional. The same functional was used for the calculation of the ^1H and ^{13}C chemical shifts of stereoisomers of poly(vinyl chloride) oligomers [20] and thermal dehydrochlorination of poly (vinyl chloride) [14]. The harmonic vibrational frequencies have been checked for the optimized structures to confirm that the true energy minimum has been found. Both infra-red and Raman harmonic vibrational modes were calculated and uniformly scaled by a factor of 0.98 [21]. The simulated spectra were calculated to the PVC and DEHA models followed by a $10\,cm^{-1}$ half-width convolution.

3. Results and discussion

3.1. Molecular model and structure

To obtain the calculated vibrational spectra, PVC and the plasticizer DEHA conformational structures were optimized by employing DFT calculations and the minimum energy conformations were presented in Fig. 2. The structural composition of PVC polymer is linear and composed of monomers that are mainly arranged in a head-to-tail with chloride on alternating carbon centers. The PVC in its crystalline form belongs to the space group $P_{cam} - D_{2h}$ with measured bond distances of 1.53 Å for C–C, 1.76 Å for C–Cl and 1.10 Å for the C–H bond [22,23].

In our model we choose the dimer conformation (CH_3-CC_2Cl) as the repeating unit with the hydrogen atoms saturating the carbon atoms bonds as presented in Fig. 2. The conformation of the minimum energy of the PVC monomer is sketched in Fig. 2 with bond values of 1.52 Å, 1.81 Å and 1.11 Å respectively for C–C,C–Cl and C–H bonds. Previous calculated values with the B3LYP functional by Wang et al. [14] obtained 1.832 Å for the C–Cl bond and 1.517 Å for the C–C distance.

For the DEHA we used the same calculation methods as used in PVC ones. The DEHA is in linear conformation at minimun energy and consists of 42 hydrogens, 22 carbons and 4 oxygen atoms, resulting in a total of 68 atoms.

3.2. FT-IR

The main absorption bands for the PVC film are in accordance with the bands found by previous authors [3,24]. The FT-IR spectrum of PVC film showed peaks for C–H bond stretching for CH_3 and CH_2 groups between 3000 and $2800\,cm^{-1}$, angular deformation for CH_2–Cl bond at $\approx 1400\,cm^{-1}$, deformation for methylene groups at $\approx 1350\,cm^{-1}$, out of plane angular deformation of Cl–CH bond at $\approx 1250\,cm^{-1}$,